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Modification of Acetyl Acetone with Methyl Acrylate

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Abstract

Acetyl acetone was modified by a KF/alumina mediated Michael addition reaction under solventless condition with methyl acrylate. Methyl acrylate formed single and double addition with the acetyl acetone. The optimal temperature for this reaction was 393 K. The modified β-diketones were confirmed using GC-FID and GC-MS. The products could be tested as metal chelating agents and in related applications.

Keywords

Michael Addition, Neat Condition, β-diketones, Heterogeneous Catalysis

1. Introduction

Although β-diketones are useful metal chelating agents, modifying them with carboxylate groups could enhance their metals chelation capacity. The modification of β-diketones such as acetyl acetone and dibenzoylmethane with saturated and unsaturated organic halide has long been reported [1]–[3]. The alkylation of acetyl acetone with isopropyl alcohol in the presence of boron trifluoride has also been previously carried out [4]. Ferrari *et al.* [5] modified acetyl acetone with tert-butyl bromoacetate using sodium hydride in THF at room temperature for about 24 h to form tert-Butyl-3-acetyl-4-oxopentanoate [5]. Consequently, unsaturated (α, β) carbonyl esters can be added to α-position of β-diketones using the Michael addition reaction and then hydrolyse the modified β-diketones for enhancing the chelation ability as has been suggested by [6]. One possibility of modifying acetyl acetone with unsaturated esters is by using Michael addition. Moreso, neat Michael addition reactions have recently been reported [7]. Hence KF/alumina has find use as an effective solid heterogeneous base catalyst for effecting Michael addition reaction and many other reactions [8], [9]. This catalyst has attracted widespread interest because it is convenient and environmentally-benign [10], [11]. This modification will form zero nitrogen content chelating molecules as it is currently desired of greener chelators. However little information is out there on the modification of β-diketones with unsaturated esters. Therefore, this paper deals with the modification of acetyl acetone with methyl acrylate under KF/alumina mediated Michael addition reaction.

2. Materials and Equipment

Acetyl acetone, methyl acrylate, ethanol, KF/Alumina, methanol, Perkin Elmer Clarus 500 GC coupled with a Clarus 500 quadrupole mass spectrometer, GC-FIDS Agilent 7820A (Agilent 6890N, Hewlett Packard HP6890).

2.1 Preparation of the KF/ Alumina

KF/Alumina was prepared using the procedures of Clark *et al.* [12] and Lenardão *et al.* [11]. Alumina was pre-treated by drying in oven at 423 K for 12 h. Then about 10 g of alumina was mixed with 3 g KF and dissolved in 20 mL of methanol. This mixture was subjected to stirring for 30 min at 323 K. Thereafter, methanol was removed by rotary evaporator with a constant equal mixture during solvent removal [12]. The KF/Alumina was dried in vacuum oven for 14 h at 423 K. This mixture represents 5 mmol KF/g alumina.

2.2 Facile modification of acetyl acetone with methyl acrylate

About 1 g KF/alumina was thoroughly mixed with 0.04 g acetyl acetone in a screw cap vial; 5 equivalent methyl acrylate were put into it. The system was reacted with continuous magnetic stirring for 4 h at 333 K under neat condition. The sample mixture was analyzed on GC-MS and GC-FID. The molecular ions of the products were identified as; 272 m/z (the retention time of the peak was 25 min) and 186 m/z (the retention time of the peak was 18 min) for double and single addition of the acrylate respectively.

2.3 GC-FID Analysis

GC analysis was performed using GC-FIDS Agilent 7820A (Agilent 6890N, Hewlett Packard HP6890) with RXI-5HT column, and column diameter of 30 m x 0.25 mm x 0.25 µm nominal was fitted with constant pressure of 22.35 psi; column maximum temperature of 673 K. The carrier gas used was helium. The samples were injected by automated injection (1 µL injection volume) with injection temperature, 563 K and a split ratio of 50:1. Oven condition; starts 323 K for 4 min, ramp at 283 K/min and finally reaches 563 K to hold for 10 min. The detector temperature was set to 613 K. The total time of the method was 38.0 min. 20 mg of sample in 1 mL ethanol was used in this analysis.

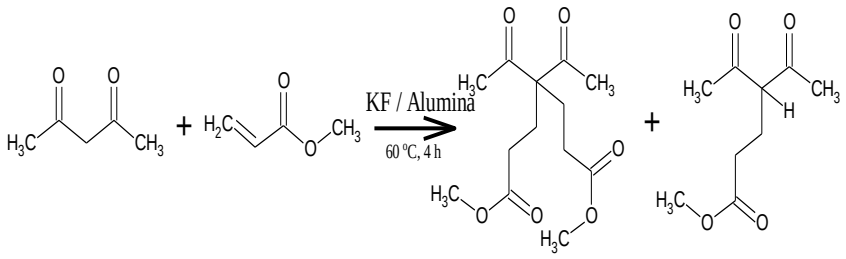
2.4 GC-MS Analysis

Mass spectra analysis was carried with 20 mg of the sample in 1 mL ethanol on a Perkin Elmer Clarus 500 GC coupled with a Clarus 500 quadrupole mass spectrometer. The GC-MS was fitted with a DB5HT capillary column (30 m x 0.25 mm x 0.25

μm nominal) with pressure of 22.35 psi carrier gas (helium). The temperature of the injector was 573 K and the flow rate was set to 1.2 mL/min. The initial oven temperature was maintained at 333 K for 1 min. The temperature was then ramped at a rate of 281 K/min until 633 K and held for 10 min. The Clarus 500 quadrupole mass spectrometer was operated in the electron ionization mode (EI) at 70 eV, a source temperature of 573 K, quadrupole at in the scan range of 30 - 1200 amu/sec. The data was collected with the PerkinElmer enhanced TurboMass (Ver5.4.2) chemical software and compounds were identified by analyzing the mass fragmentation patterns and comparison of mass fragmentation patterns with spectra contained in the NIST library (v. 2.2).

3. Results and Discussion

The methyl acrylate was effectively added onto acetyl acetone. Moreso, there was complete conversion of the acetyl acetone into the Michael adduct. Therefore, single and double addition of the methyl acrylate were formed as it is described in Figure 1 and 2 with the GC MS and chromatogram. The detail reaction of the modification is described in Equation 1.



Equation 1: Modification of acetyl acetone with acrylate

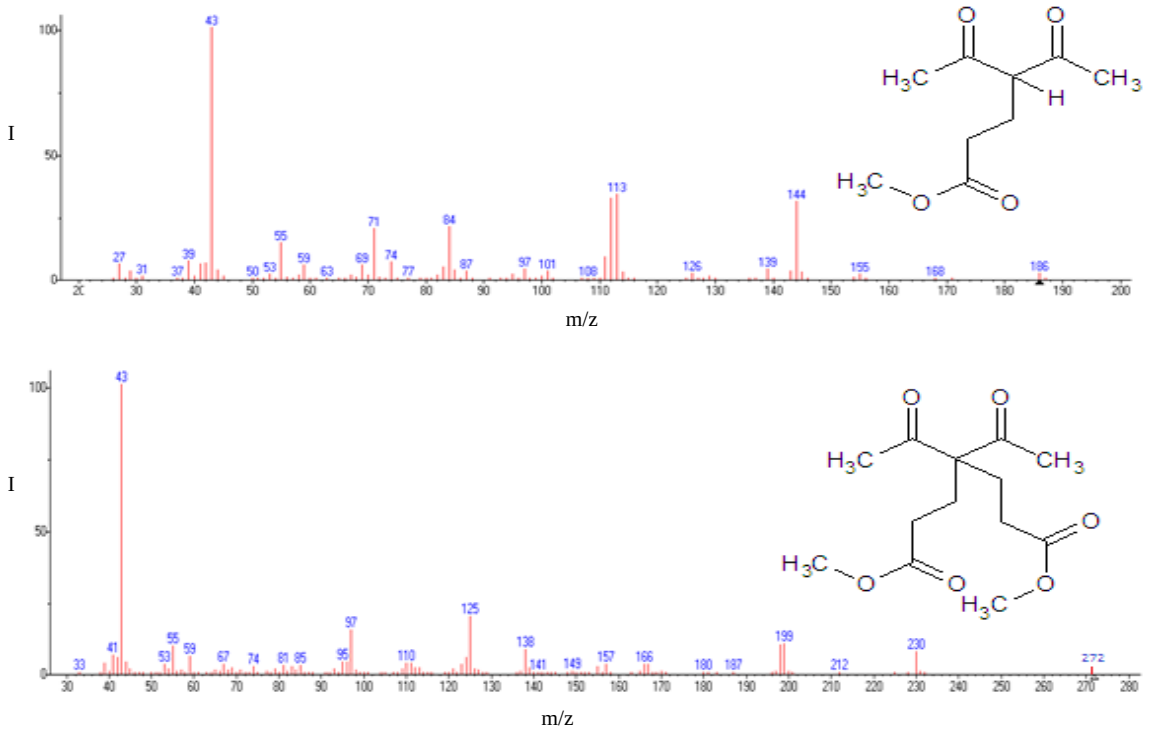


Figure 2: GC-MS for the products – *Note, I = intensity*

I

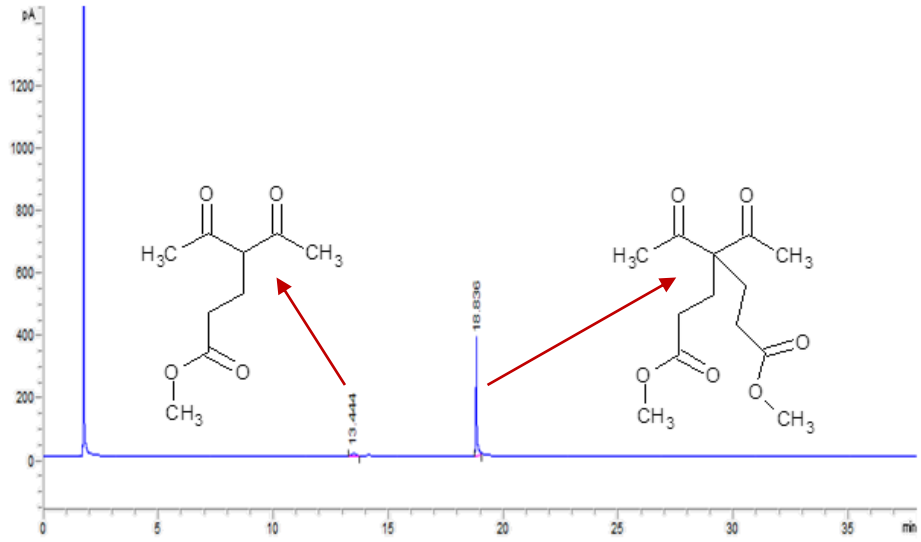
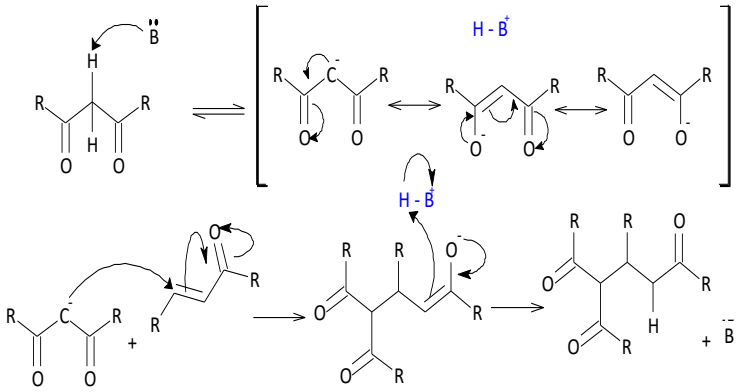


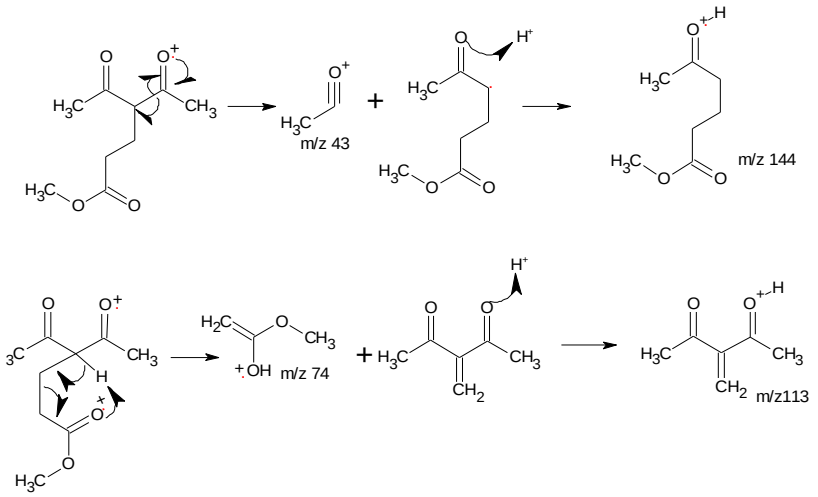
Figure 1: GC-FID chromatogram for the products

The *α*-protons in the β-diketone are acidic and can be removed by relatively weak bases including; ammonia, sodium hydroxide, piperidine or pyridine; but a much stronger base is required for the second deprotonation [13]. Thus advantage is taking of the acidic nature of β-diketone to effect the modification.

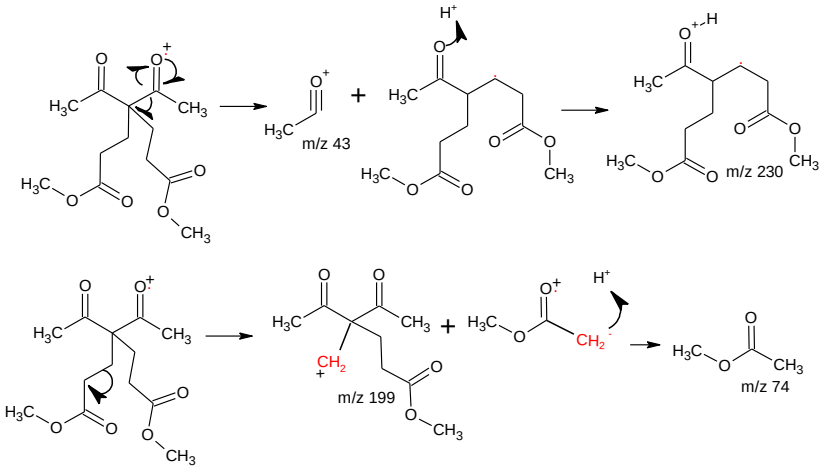
KF/Al_2O_3 mediated modification of acetyl acetone with methyl acrylate was carried out in solventless condition in accordance with the 1st and 5th principle of green chemistry so as to minimize waste and unnecessary use of solvents. Double and single addition of the methyl acrylate onto acetyl acetone was observed as it has been reported in similar reactions[14]. Escalante *et al.* [14] conducted Michael addition of amines to methyl acrylates under microwave irradiation and also observed double addition. The broad scheme of the Michael Addition reaction is described in Scheme 2. The reaction involves the use of the heterogeneous base catalyst KF/alumina [7]. The reaction begins with deprotonation of the β-diketone by the base [9], resulting to formation of a resonance stabilized carbanion (nucleophile). This nucleophile is then added to the electrophile (the unsaturated carbonyl moiety) and subsequently the transfer of protons from the base to the Michael product [15]. Consistent fragmentations for these single and double addition products are highlighted in Schemes 3 and 4 respectively. The fragmentation is typical of carbonyl compounds, involving McLafferty rearrangement and cleavage of C(O) – C bond [16].



Equation 2: Scheme of the Michael addition reaction



Equation 3: Proposed fragmentation pattern of the monoaddition of the acrylate product



Equation 4: Proposed fragmentation pattern of the bisaddition of the acrylate product

Michael addition reactions are often carried out in polar solvents such as methanol, acetone, DMSO, THF [5] and MeCN [17]. In the present studies, these reactions were carried out under solventless condition as similarly reported by Ravichandran and Karthikeyan [18], [7] in order to simplify the process, prevent solvent wastes, hazards, and reduce the potential toxicity [19], [20]. Solvent-free microwave mediated Michael addition has also been performed by Rao and Jothilingam [21]. They found that the solvent-free condition was better than using polar aprotic solvent such as DMSO [21]. Traditionally, large amounts of organic solvents have been used to carry out reactions in commercial processes. The solvents allow the reactants to interact and they also provide a heat sink for any energy released in the processes. Solvents can be expensive, and therefore must be recovered and reused if possible. But 100% recovery is generally impossible, and some solvent is lost as vapor or is released into the environment thus expensive pollution control measures must be in place [22]. These control measures are not 100% effective and some solvent is lost to the environment. Therefore, the solvent may become a contaminant in either soil, water, or the atmosphere [22]. The chemical profession has increasingly turned to developing “green processes” which minimize the use of toxic materials and hence the use of solvent free reactions is becoming popular [22]. It is important to note that economic feasibility of bio-derived acrylic acid is in the pipeline [23]. Methyl acrylate can in turn be obtained from the would – be bioacrylic acid. This then will be an added advantage of this reaction in terms of the Principles of Green Chemistry. Some other advantages of this reaction is predicated on the KF/alumina used. KF/alumina catalyst can be re-used up to four times without a drop in the yield through thorough washing with ethyl acetate and drying [24]. It also has mild reaction conditions, easy work-up procedure and selective synthesis of the target molecules [7].

4 Conclusion

Acetyl acetone was modified by a KF/alumina mediated Michael addition reaction under solventless condition with methyl acrylate. Methyl acrylate formed single and double addition with the acetyl acetone. The optimal temperature for this reaction was 393 K. The modified β-diketones were confirmed using GC-FID and GC-MS. The products could be tested as metal chelating agents and in related applications.

5. Acknowledgements

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6. References

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